

Chemically Bonded Cements from Boiler Ash and Sludge Wastes

**Phase II Report
(September 1998- July 1999)**

**By
Toshifumi Sugama**

**Materials and Chemical Sciences Division
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973**

Kenneth A. Yager

**KeySpan Corporation
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Shore Road, Glenwood Gas Plant
Glenwood Landing, New York 11547**

For

**Project Manager
Diane Blankenhorn
KeySpan R&D Initiative**

August 1999

The logo for KeySpan, featuring the word "KEYSPAN" in a bold, sans-serif font. A stylized, curved line arches over the letters, resembling a bridge or a stylized 'K'.

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Abstract

Based upon the previous Phase I research program aimed at looking for ways of recycling the KeySpan-generated wastes, such as waste water treatment sludge (WWTS) and bottom ash (BA), into the potentially useful cementitious materials called chemically bonded cement (CBC) materials, the emphasis of this Phase II program done at Brookhaven National Laboratory, in a period of September 1998 through July 1999, was directed towards the two major subjects: One was to assess the technical feasibility of WWTS-based CBC material for use as Pb-exchange adsorbent (PEA) which remediates Pb-contaminated soils in the field; and the other was related to the establishment of the optimum-packaging storage system of dry BA-based CBC components that make it a promising matrix material for the steam-cured concrete products containing sand and coarse aggregate. To achieve the goal of the first subject, a small-scale field demonstration test was carried out. Using the PEA material consisting of 30 wt% WWTS, 13 wt% Type I cement and 57 wt% water, the PES slurry was prepared using a rotary shear concrete mixer, and then poured on the Pb-contaminated soil. The PEA-to-soil ratio by weight was a factor of 2.0. The placed PEA slurry was blended with soil using hand mixing tools such as claws and shovels. The wettability of soils with the PEA was very good, thereby facilitating the soil-PEA mix procedures. A very promising result was obtained from this field test; in fact, the amount of Pb leached out from the 25-day-aged PEA-treated soil specimen was only 0.74 mg/l, meeting the requirement for EPA safe regulation of < 5 mg/l. In contrast, a large amount (26.4 mg/l) of Pb was detected from the untreated soil of the same age. Thus, this finding demonstrated that the WWTS-based CBC has a potential for use as PEA material. Regarding the second subject, the dry-packed storage system consisting of 68.7 wt% BA, 13.0 wt% calcium aluminate cement (CAC), 13.0 wt% Type I portland cement and 5.3 wt% sodium polyphosphate (NaP), was designed in response to the identification of the most effective CBC formulation in strengthening the steam-cured concrete specimens. Using this storage system with the material cost of 6.32 $\text{\$/lb}$, the 80°C-20 hour-steam-cured concrete specimens displayed the compressive strength of 3980 psi, tensile splitting of 416 psi, flexural strength of 808 psi, and modulus of elasticity of 3.16×10^6 psi. Furthermore, the specimens had a good resistance to acid erosion and a lower permeability of water, compared with those of the conventional Type I cement concrete specimens. Consequently, the cost-effective BA-based CBC gave the promise of being a

potentially useful material for fabricating high-performance precast concrete products, such as building blocks, pipes, and slabs.

1. Introduction

According to KeySpan, the annual accumulation of waste water treatment sludge (WWTS, ~ 35 wt% solid sludge) and boiler ash (BA) waste generated in their power plants was projected to be ~ 2400 wet tons and ~ 270 tons in 1999, respectively. These wastes contain heavy metals such as vanadium (V) and nickel (Ni), and must be disposed of in accordance with New York State's hazardous waste regulations. The annual cost for their collection and disposal was estimated to be ~ \$ 200,000. These facts have driven KeySpan to look for ways to recycle these wastes into potentially useful materials, and concurrently reduce the costs associated with their disposal. Also, KeySpan is interested in developing explicit strategies to integrate industrial ecology and green chemistry.

Another environmental issue confronting KeySpan was the contamination of soil brought about by lead (Pb) pigment present in the paint fragments which flake off from high voltage towers and their facilities. Although only the superficial layers of soil were contaminated, such sites must be cleaned up to eliminate any risk to the environment. Currently, there are three technologies to remedy polluted sites [1]; 1) hauling the contaminated soil to a landfill and replacing it with clean soil, 2) chemically immobilizing and stabilizing Pb, and 3) leaching out the metals with a soil-washing method using acids. The second technology is of particular interest to us in immobilizing Pb into solid and inert forms. An important requirement contributing to the success of this strategy is that the solid forms must have excellent stability, so that they retain toxic Pb even when exposed to potential leachants.

Based upon this information, the research program at Brookhaven National Laboratory (BNL) sponsored by KeySpan is aimed at alleviating environmental concerns, reducing the disposal costs of these wastes, and developing process technologies that recycle these harmful wastes into commercially viable products. The program also seeks potential applications for them with the economic benefits that may accrue from selling the end-use products. BNL's

approach to achieving these goals is to focus on synthesizing and formulating chemically bonded cement (CBC) from these WWTS and BA wastes, to assess their abilities to immobilize Pb in the contaminated soil, and to use them as binders in building and civil engineering materials. The first CBC material, called Pb-exchange adsorbent (PEA), is used for remediating Pb-contaminated soil; the second one, called high-performance cement (HPC), provides CBC-based concrete for potential use in KeySpan precast products, such as building blocks and pipes. In addition, both PEA and HPC materials must be able to intercalate and encapsulate the V and Ni metals present in the raw WWTS and BA wastes.

In July 1998, we started a two-year research and development program which centered on exploring methods to recycle these wastes into potentially useful ones. To date, one annual progress report as the Phase I research program [2] was issued in August 1998 and covered the results of all the work performed to the end of July 1998. The principal findings described in this previous report are summarized as follows: We synthesized CBC with three specific characteristics; 1) the ability to immobilize hazardous heavy metals, such as Pb, Ni, and V, 2) rapid hardening and setting properties, and 3) the development of high mechanical strength. The CBCs were prepared by an acid-base reaction between these by-products acting as the solid base reactants and the sodium polyphosphate solution as the cement-forming acid reactant, followed by a hydrating reaction. Two additives, the calcium aluminate cements (CAC) and the calcium silicate cements (CSC) were incorporated into the CBC systems to improve their properties. Using a CBC formulation consisting of 54.0 wt% WWTS, 23.0 wt% CSC, and 23 wt% [40 wt% $-(\text{-NaPO}_3\text{-})_n$], the Toxicity Characteristics Leaching Procedure (TCLP) tests showed that only minimal concentrations of Pb, Ni, and V metals leached out from the specimens. Also, CBC specimens derived from a formulation consisting of 42 wt% BA, 18 wt% CAC and 40 wt% [40 wt% $-(\text{-NaPO}_3\text{-})_n$] displayed an excellent compressive strength of 1500 psi during the early curing age of 2 hours after mixing at room temperature. The reason for its rapid hardening was due to a high exothermic energy evolved by the acid-base reaction. Furthermore, when these specimens were immersed for 28 days in water at 25 °C, and exposed for 20 hours to steam at 80°C, a very high compressive strength of > 4000 psi developed.

Thus, we identified the potential of WWTS waste for use as the major component in the PEA material systems that tightly binds or sequesters most of the heavy metals. Since BA is capable of strengthening CBC specimens, there was no doubt that this waste could be applied to HPC materials.

2. Project Objective

The most promising formulations of CBC for WWTS-based PEA and BA-base HPC materials were optimized in the Phase I research program. Accordingly, the overall objectives of the current program were twofold: 1) to apply PEA material to Pb-contaminated soils and to develop its placement technologies, and 2) to design and characterize HPC-based concretes containing sand and coarse aggregate, which have a high potential for use as precast products.

A near term benefit of this research for KeySpan is that it will offer potential applications and markets for using these wastes, thereby reducing the costs associated with their disposal while alleviating the environmental impact. The work described in this Phase II report began in September 1998 and was completed in July 1999. This work consisted of three tasks:

Task 1. Assessment of the uptake of Pb Ions and Selectivity Other Cations by PEA

Task 2. Optimization of HPC-based Concrete Formulations

Task 3. Cost Estimate of Materials

3. Experimental

Two raw waste materials, WWTS and BA acting as base powder reactants, were supplied by KeySpan. The "as-received" WWTS contained free water of ~ 65 wt%. The BA was a rock-like hard bulky solid, and was powdered using a crusher (Retrch Type BB1A, Brinkmann, Co.). The distribution of particle size for the crushed BA was given in Figure 1. A granular polybasic sodium phosphate, $[-(\text{NaPO}_3)-]_n$, (Aldrich Chemical Company)], known as an intermediate of

fertilizers, was used as the acid reactant. Two cement additives, Refcon as calcium aluminate cement (CAC) and Type I as calcium silicate cement (CSC), were obtained from the Lehigh Portland Cement Company. The X-ray diffraction (XRD) analyses showed that the major chemical components in the CAC were composed of monocalcium aluminate, monocalcium dialuminate, and gehlenite; the principal component of CSC was tricalcium silicate. These additives were used to accelerate the acid-base reaction and to improve the mechanical strength of CBC.

The leachability of the hazardous heavy metals such as Pb, Ni, and V, from the solidified binder matrix was detected by the Toxicity Characteristics Leaching Procedure (TCLP) recommended by the U.S. Environmental Protection Agency (EPA). The concentrations of Pb, Ni, and V ions in the leachates were determined by atomic absorption spectrophotometry (AA). Table 1 shows the elemental composition of BA, which was analyzed by the KeySpan System Laboratory. As is seen, the BA included three major ingredients, calcium (Ca), magnesium (Mg), and vanadium (V), in concentrations ranging from 86700 to 35700 mg/kg. The second highest levels, in the range of 12000-11600 mg/kg, were detected for iron (Fe) and nickel (Ni), while the copper (Cu) and zinc (Zn) ranged from 3070 to 1610 mg/kg. Also, the analytical data indicated negligible amounts (< 1000 mg/kg) for arsenic (As), barium (Ba), lead (Pb), and manganese (Mn). This information was supported by x-ray powder diffraction (XRD) analysis, in a d-spacing range from 0.134 to 0.225 nm. The XRD results revealed that BA contains two major chemical compounds, CaSO_4 and $\text{V}_2(\text{SO}_4)_2$. Similar analytical results were obtained from the WWTS, except for the inclusion of a substantial amount of polyacrylamide as a chelating additive for Ni and V.

4. Results and Discussion

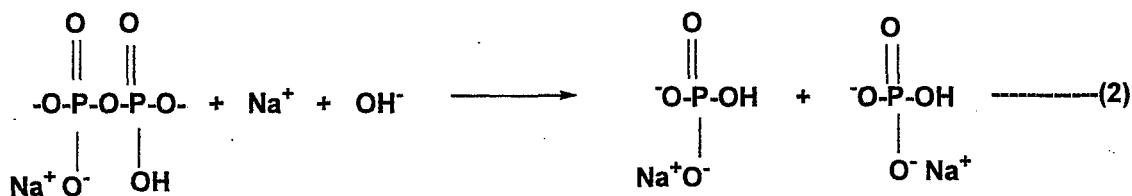
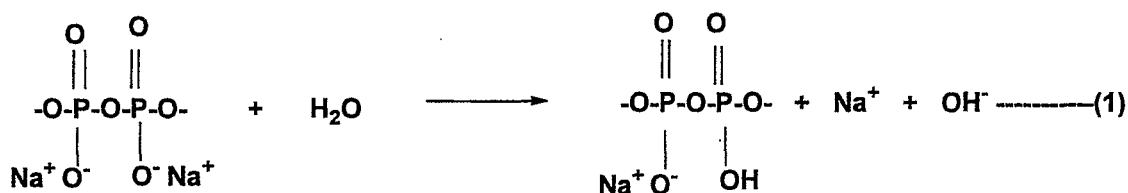
4.1. Pb-exchange Adsorbents (PEA)

The most promising PEA system consisted of three components, the waste water treatment sludge (WWTS), Type I portland cement, and sodium polyphosphate (NaP). Therefore, five PEA formulations, as shown in Table 2, were employed in this study, and mixed directly with Pb-contaminated soil that was transported from KeySpan sites. The specimens were prepared in accordance with the following sequence: First, the proper amount of NaP solution

was incorporated into the WWTS, and then mixed in thoroughly by hand until the bulky WWTS mass was completely wetted and dispersed in this NaP solution; second, Type I cement was added to the WWTS-dispersed NaP solution; finally, the soil was mixed with the PEA slurries consisting of WWTS, Type I cement, NaP, and water. After mixing, the slurries were cast into molds (3 in. diam. x 6 in. long), and allowed to harden for 7 days at room temperature. These 7-day-aged specimens were sent to KeySpan System Laboratory (Mr. Yager) for the TCLP tests that gave us information on the ability of the PEAs to immobilize hazardous heavy metals, such as Pb, V, and Ni.

Table 3 shows the results of TCLP leachability and compressive strength tests for these specimens. As expected, the compressive strength of the specimens was enhanced with an increasing concentration of NaP in the WWTS-based PEA material. The specimens made with 40 wt% NaP had a compressive strength of 220 psi, corresponding to eleven times more than that of the specimens without NaP. Of particular interest was the fact that the ability of PEA to immobilize these hazardous heavy metals was independent of their mechanical strength. Although all the specimens were highly effective in sequestering Pb and Ni metals, the leachability of V metal depended primarily on the concentration of NaP; namely, increasing the concentration of NaP resulted in a lower efficiency on immobilizing V ions.

As is known [3], the hydrolysis of NaP in aqueous medium takes place in the following two stages:



The Na^+ ion in the hydrolysate of NaP is capable of exchanging with most of the heavy metals, allowing the NaP to form the lead phosphate hydrate, $\text{Pb}(\text{HPO}_4) \cdot x\text{H}_2\text{O}$, as the ion exchange reaction product between Na^+ in the hydrolysate and Pb^{2+} in the soils. However, such strong ion exchangeability of the hydrolysate seems to extract the Ni and V ions from their chelating polyacrylamide complexes, so liberating free Ni and V ions. This may be the reason why the incorporation of a large amount of NaP into the Pb-contaminated soil led to an increasing leachability of Ni and V from the PEA specimens. Since the ideal PEA not only must immobilize Pb, but also must efficaciously sequester the other heavy metals such as Ni and V, contained in the WWTS, these data strongly suggested that a PEA system composed of 30 wt% WWTS, 13 wt% Type I cement, and 57 wt% water, without NaP, was recommended as the most effective one in immobilizing all these heavy metals. We assumed that its effectiveness might be due to the combination of two different functions: One is that an excessive amount of polyacrylamide polymer additive in the WWTS has a strong chemical affinity for all these metals to bind tightly or sequester them; the other is the encapsulation and intercalation of Pb-, V-, and Ni-complexed polyacrylamide by the Type I cement hydrates.

Using this PEA formulation, emphasis next was directed towards a small-scale field demonstration test in the molds (4 ft. x 4 ft. x 0.8 ft.) at the KeySpan System Laboratory site in Glewood Landing. This field test aimed to ascertain that the results of the in-house studies can be duplicated in the field and also to develop the placement technologies for PEA. The PEA was prepared and placed in accordance with the procedures described below:

A. Preparation of PEA

Prior to preparing the PEA, 186 lbs of Pb-contaminated soil were placed in each of two molds (Figure 2). For the purpose of comparison, soil that was not treated with PEA was placed in the left side of mold (see Figure 2.). 37.0 lbs of raw WWTS was removed from its storage drum (Figure 3), and poured into a rotary shear concrete mixer (Figure 4). Since the raw WWTS often coalesce into lumps of mud, we rotated the mixer for at least 3 min to break up this enjoined material (Figure 5). Following this, 40.0 lbs of water were added to the WWTS mud,

and then mixed for ~ 5 min to make a smooth suspension. Next, 15.8 lbs of Type I portland cement were incorporated into the mud suspension, and mixed for approximately 3 min (Figure 6). After mixing, we observed that adding cement increases the consistency of the mud slurry. Since an ideal mud cement slurry must have a low viscosity and possess a self-leveling characteristic, we charged an additional 25 lb water into the mud cement slurry, and mixed it for a further 3 min. Visual observations revealed that a mixing time for 3 min is enough to make a self-leveling mud cement slurry.

B. Placement of PEA

The slurry was discharged from the mixer into a plastic pail (Figure 7), and subsequently poured on the surface of the Pb-contaminated soil (Figure 8). This process of preparing PEA was repeatedly carried out for another two times, so that 353.4 lbs of PEA were placed on the soil's surface.

C. Blending the PEA with the Soil

The placed PEA slurry was blended into the soil in the mold using hand mixing tools such as a claw and shovel (Figure 9). The wettability of soil with the PEA was good, therefore, the time needed to completely mix the soil and PEA was only 5 min. Afterward, a polyvinyl sheet was laid over the PEA-treated soil and it was left for 7 days. The cover prevented the volatilization of moisture from the treated soil, and the incorporation of more water into the treated soil during heavy rain falls; it also aided in promoting the degree of hydration of the cement.

D. Infield Leachability Tests

After 7 days, the polyvinyl sheet was removed from the surface of the treated soil. The specimen showed clay-like structure and feature. To demonstrate that this chemical immobilization technology can clean polluted sites and prevent migration of the lead, we scratched the surface with a claw (Figure 10), and exposed it to water from a sprinkler to simulate rainfall. The solution that percolated through the soil was collected by opening a drain pipe attached to the bottom corner of the mold, and was tested for the amount of Pb, Ni, and V

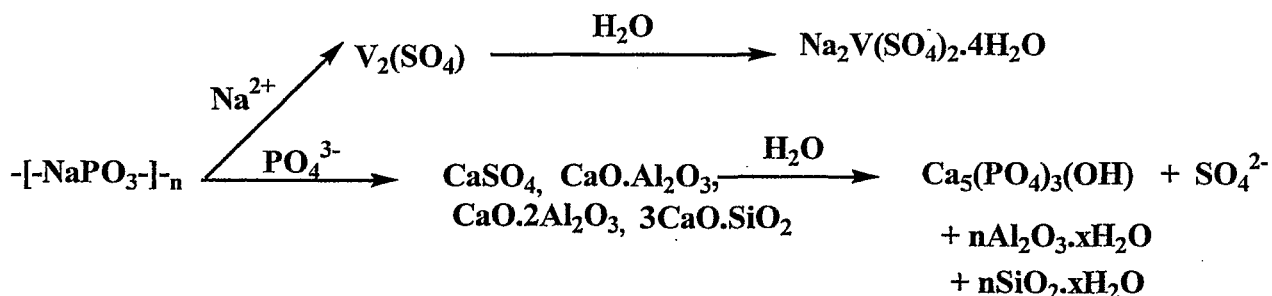
metals that leached out from the treated soil. Table 4 shows the results from the leaching testing of Pb, Ni, and V metals for the 25-day-aged PEA-treated and untreated soil specimens after field placement. As expected, PEA markedly acted to immobilize the Pb metals; in fact, the Pb concentration of 26.4 mg/l leached out from the untreated soil fell by 97.6 % to 0.74 mg/l in soils containing PEA. The EPA's safety limit for leaching Pb is < 5 mg/l, so the value of 0.74 mg/l was far below, demonstrating that the Pb-contaminated soil was mediated by the WWTS-based PEA materials. As described in the Phase I report [2], the raw WWTS contained a large amount of V (53000 mg/kg) and Ni (30000 mg/kg). It is not surprising that only negligible amounts of these metals were detected in the percolated solutions. However, the question of the PEA's useful lifetime for dealing with Pb remains unanswered. The other intriguing question was whether this chemical treatment technology can support life forms in the ground and contribute to restoring the soil. It is well documented [4] that, using the soil-washing technology in which the soil is mixed with acid to strip off the metals, such soil cleanup treatments do not guarantee that the remediated sites can support wildlife or farming because the treatment with acid kills soil microorganisms and takes away organic nutrients, essentially for no growth of plants. To answer this question, we planted lawn grass, vegetables, and small shrubs in treated soil. Because the plants absorb toxic metals from polluted soil and water, such plantings may further alleviate the problem of soils containing toxic metals.

Figure 11 shows the extent of growth of these plants in the untreated and treated soils nearly one month after planting. A well-grown plant can be seen in the untreated site (left side in the photograph). By comparison, the treated soil (right side) seems to inhibit the growth of plants; in fact, the roots of the lawn grass did not spread deeply into the soil, and they could be pulled out easily. Unfortunately, this finding suggested that there was a need to incorporate fertilizers and organic nutrients into the treated soils to aid the growth of plants.

4.2. High-performance Concrete

In the previous Phase I work, we studied the characteristics of the CBC specimens derived from the bottom ash (BA)-calcium aluminate cement (CAC)-NaP systems. The consequent data showed that the CBCs have high potential for use as HPCs, offering high mechanical strength, quick-setting characteristics, and a binding matrix for V and Ni metals

present in the BA. Since the CAC additive acts to promote the rate of acid-base reactions, incorporating the base reactant with 70/30 BA/CAC ratio into the $-(\text{NaPO}_3)_n$ acid reactant generated a high exothermal reaction energy, leading to rapid hardening and setting. In fact, the cement slurry was converted into a solid state within the first ten minutes after mixing. The excellent compressive strength of > 4000 psi for this cement system was attained when the cement specimens were cured by exposing them for 20 hours in 80°C steam. Two important factors played a key role in providing such a high compressive strength: One was the formation of both well-crystallized hydroxyapatite [HOAp, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] and sodium vanadium sulfate hydrate [SVSH, $(\text{Na}_2\text{V}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O})$] in the cement bodies; the other was associated with the development of densified cement microstructure. These reaction products may be formed by the following hypothetical reaction mechanisms:



First, the Ca cations liberated from the BA and CAC have a strong chemical affinity for the phosphate anions dissociated from the $-(\text{NaPO}_3)_n$ acid solution, leading to the formation of calcium phosphate compounds. Second, Na cations as the counter anions of phosphate ions favorably reacted with $\text{V}_2(\text{SO}_4)_3$ present in the BA to yield the sodium vanadium sulfate compounds. Finally, the hydration of these reaction products contributed to promoting their crystallization, thereby developing a dense microstructure in the CBC. In this mechanism, three compounds, SO_4^{2-} , $n\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, and $n\text{SiO}_2 \cdot x\text{H}_2\text{O}$, may be formed as by-products in this acid-base-hydration reaction process.

Based upon this information, emphasis next centered on establishing the optimum-packed storage system of dry cement components that bind the sand and coarse aggregate into a cohesive mass. Two factors were important in attaining this goal: One was to obtain the best compressive strength in the steam-cured cement concrete specimens; the other was related to estimating the costs of the packaging components. Further, we investigated the mechanical and physical properties of the concrete specimens made with a cost-effective dry cement packaging. For the purpose of comparison, conventional Type I cement-based concrete specimens were also used.

4.2.1. Standard Cement Packaging

The eight concrete formulations (Table 5) were designed to define an appropriate CBC binder/aggregate ratio for developing a high mechanical strength in the concrete specimens. The particle sizes of silica-based coarse and fine aggregates used in this work ranged from 9.5 to 2.4, mm and from 1.2 to 0.15 mm, respectively. In preparing the specimens, a dry mixture consisting of crushed bottom boiler ash (BA), non-crushed boiler ash (NBA), calcium aluminate cement (CAC), and aggregate was incorporated into a 40 wt% NaP solution, and then mixed by hand for 3 min. After mixing, concrete slurries were cast in cylindrical molds (3 in. diam. x 6 in. long) and left for 24 hours in an atmospheric environment. Following this, the specimens were removed from molds and exposed to steam for 12 hours at 80°C to determine their compressive strength. The results from these specimens are shown in Table 6. The data indicated that the compressive strength of the specimens depended primarily on the binder/aggregate ratio and the species of boiler ashes. The most effective binder/aggregate ratio in developing a high compressive strength of the specimens was a 50/50 by weight. The increase in the proportion of binder to aggregate caused a decline of strength. The data also represented that the specimens made with the BA was much stronger than those made with NBA-derived concretes.

Considering the practical applications of dry packed cements, the ideal packaging is to include all three cement-forming components, BA, CAC, and NaP, so that the extent of the slump of the cement concrete slurry can be controlled by directly adding an appropriate amount of water to the dry concrete mixtures. Accordingly, four formulations of dry mix

cement/aggregate packaging (Table 7) were designed and prepared in a powder rotary mixer. For all dry packed formulations, 10 % water by weight of the total amount of dry cement/aggregate mixture was incorporated to make cement concrete slurries. The slurries were prepared by mixing them for 3 min in a small concrete mixer, and then cast in cylindrical molds (3 in. diam. x 6 in. long). The casted concrete specimens were left for 24 hours in an atmospheric environment. Following this, the specimens were removed from molds, exposed in steam for 12 hours at 80°C, and then tested for determining the compressive strength. The results from these specimens are shown in Table 8. The compressive strength of the specimens depended mainly on the concentrations of NaP in the dry mixed formulations; namely, a 7 wt% NaP was responsible for developing the highest compressive strength of 3650 psi; beyond this concentration, strength seems to decline.

Using the formulation given in Table 9, emphasis next centered on investigating the changes in compressive strength of the concrete specimens as a function of curing time in water at 25°C and steam at 80°C. For the comparison purpose, the commercial Type I cement-based concrete specimens were also prepared as reference. The formulation of Type I cement-based concrete slurry also is shown in Table 9. As is seen, the major characteristic of the BA-based concrete's formulation was the lesser amount of water added to the dry concrete mixture, than that of the reference specimens; namely, only 8.5 wt% of water needed to obtain a desirable slump of the concrete slurry. Table 10 gives the results of the compressive strength tests. As expected, for both the BA-based concrete and reference concrete specimens cured in water, the compressive strength tends to increase with an extending curing time. The maximum strength of these specimens after being submerged for 28 days in water was almost the same as those of the specimens cured in steam for 12 hours. Nevertheless, the maximum strength of the BA-based concretes was ~ 8 % higher than that of the Type I cement concretes.

Although the BA-based cement concretes displayed excellent mechanical strength, the question of their economical feasibility is unanswered. There is no doubt that the key to successful application of this dry-pack cement is to formulate a cost-effective cement system with a high mechanical strength. Most of the work done to date has centered on investigating the

changes in the compressive strength of the specimens as a function of the concentration of each components in the concrete system and of the curing time. Little work has yet been devoted to relating the material cost of cement to its mechanical behavior. The material cost may be critical in some applications.

In response to these questions, the nine dry pack cement formulations (Table 11) were designed, and then their economical feasibility was evaluated by comparing the estimated material costs and the determined compressive strengths of the specimens. The cost (0.6 ¢/lb) of BA powder indicated in Table 11 was computed from the difference between the expense (4.35 ¢/lb) of crushing down bulk raw BA to fine powder and the disposal fee (3.75 ¢/lb) of BA. Since the commercial Type I portland cement costs around 6.0 ¢/lb, a cost of < 7.0 ¢/lb is desirable for BA-based cements. As is seen, five formulations, (the specimens No. 5, 6, 7, 8, and 9), in this test series, meet the criterion for cement cost. Table 12 shows the compressive strength of these neat cement specimens without aggregates cured in steam for 12 hours at 80°C. As a result, the most effective formulation of BA cements in reducing the material cost and in developing a high compressive strength was the specimen No. 5 with 68.7 wt% BA, 13.0 wt% CAC, 13.0 wt% Type I cement, and 5.3 wt% NaP. This cement which costs 6.32 ¢/lb had a compressive strength of 4620 psi, corresponding to 1.5 times higher than that of the commercial Type I cement specimens. Despite the attractiveness of this cement for use as a binder of the precast concrete products, one important consideration was that the setting time of the cement mixed with a proper amount of water at room temperature is too short to allow it to be placed in the molds because the inclusion of Type I cement additive promotes the reaction of BA cement. Of course, the kinetics of the reaction depend on the surrounding temperatures; namely, at a lower temperature, the cements would set slowly. However, at 25°C, this cement set in 3 min 15 sec, including a 1 min mixing period. Thus, cement admixtures that retard its setting time need to be developed.

For this purpose, the polyborax (PB) granular was applied as a set-retarding admixture to the BA cement slurry. The PB retarder in 2.5, 3.5, and 6.0 % by weight of the total weight of dry-pack cement mixture was dissolved in the water, and then mixed with the dry cement. Table 13 shows the changes in the setting time of the cement slurries as a function of PB concentration.

Also, the compressive strength of the retarded cement specimens after exposure for 12 hours in steam at 80°C is given in Table 13. The PB admixture was very effective in delaying the setting time of the cement slurries. With 6.0 wt% PB, its setting time was extended to 20 min. There was no significant difference in the compressive strength of the slurry specimens containing the PB concentrations of up to 3.5 wt%. However, the incorporation of 6.0 wt% into the slurry seems to cause a loss of strength.

4.2.2. Mechanical and Physical Properties

Using the optimized dry cement packaging (Table 14), we prepared the concrete specimens containing coarse aggregate (size, 9.5 to 2.4 mm) and fine aggregate (sand, size, 1.2 to 0.15 mm) by exposing them in steam for 12 hours at 80°C. The steam-cured BA cement concrete specimens were then tested for compressive strength (size of specimen: 3 in. diam. x 6 in. length cylinder), flexural strength (size of specimen; 4 in. x 4 in. x 16 in. beam), tensile splitting (size of specimen; 3 in. diam. x 6 in. length cylinder), and modulus of elasticity (size of specimen; 3 in. diam. x 6 in. length cylinder). For the flexural test, the beam specimen supported on a 12 in. span was subjected to bending under center loading, following ASTM C 292-68. In the tensile splitting test, the cylindrical specimen was placed with its axis horizontal between the plates of a testing machine, and the load was increased until failure by splitting along the vertical diameter takes place. The modulus of elasticity measurement was made, using electrical resistance strain gauges bonded to cylindrical specimen. The cylinder was loaded in compression. In addition, the water absorption, and resistance to chemical attack by 6 % H₂SO₄ and 6 % NaOH were measured. Table 15 shows the formulations of the BA-based cement concrete specimens. For the comparison purpose, the commercial Type I portland cement concrete specimens were also prepared under the same steam-curing condition, and their formulation is also given in Table 15. Table 16 compares these mechanical properties of 80°C steam-cured BA and Type I cement concrete specimens. The BA-based concrete specimens displayed a better mechanical behavior than those of the commercial Type I cement concrete specimens. The water absorption test was conducted by immersing them for up to 7 days in water at 25°C (Table 17). The results suggested that the BA concrete specimens have a better waterproof property, compared with that of the commercial Type I specimens. In fact, the water

absorption of 8.25 wt% for the 7 day-immersed BA specimens was 38 % lower than that of the comparably tested Type I specimens. To measure resistance to acid attack, these specimens were immersed for up to 10 days in 6 % H_2SO_4 at room temperature. The loss in weight of the specimens by acid erosion is given in Table 18. Although both the BA and Type I specimens suffered acid erosion at some different degrees, the BA specimens showed a better resistance. The loss in weight of the BA specimens after 10 day immersion was only 2.8 %, corresponding to as much as 68 % less than that of the Type I specimens. When the BA specimens were exposed for 10 days to 6.0 % NaOH, they had a weight loss of 0.46 %. In contrast, the Type I specimens had a weight gain of 0.29 %.

From this information, the following statement can be made: By comparison with the commercial Type I cement concretes, the BA-based concretes developed in the current program had good mechanical strength, lower permeability to water, and excellent resistance to acid.

5. Conclusion

Waste water treatment sludge (WWTS)-based chemically bonded cement (CBC) was formulated for use as Pb-exchange absorbent (PEA) materials that act to remediate Pb-contaminated soils. Using an optimum formulation of PEA, a small-scale field demonstration test was carried out to evaluate its technical feasibility and to ascertain the fact that the results of in-house work can be duplicated in the field. Since the raw WWTS contains an excessive amount of polyacrylamide (PAM) electrolytes which were primarily used to bind and sequester the heavy metals present in the waste water, PAM not only played a key role in trapping Pb metal existing in the contaminated soils, but also consecutively served in sequestering the V and Ni metals present in the WWTS. As a result, the optimum formulation recommended for use as the PEA material was as follows: 30 wt% WWTS, 13 wt% Type I cement and 57 wt% water. In this formulation, the hydration products of Type I cement were responsible for encapsulating and intercalating the Pb-, V-, and Ni-complexed PAM macromolecular structure. The preparation of PEA and its placement onto the contaminated soil in the field was performed in accordance with the following sequence:

- 1) WWTS was mixed for 3 min in the concrete mixer to break up coalescent WWTS lumps.
- 2) Water was slowly added to the WWTS, and then mixed for ~ 5 min to uniformly disperse the fine WWTS particles in the water.
- 3) Type I portland cement then was mixed with the WWTS/water mixture for 3 min. Following this, additional water was incorporated into the WWTS/Type I cement/water mixture to make PEA slurry.
- 4) A well-mixed PEA slurry was poured onto the surfaces of the previously placed Pb-contaminated soil, and they were blended using the claws and shovels as mixing tools.

The results from this field test revealed that the PEA material significantly contributes to sequester Pb metals in the soil; in fact, the amount of Pb leached out from the 25-day-aged treated soil was only 0.74 mg/l, meeting the requirements for EPA's safety regulation of < 5 mg/l. However, this chemical treatment technology did not guarantee that remediated sites can support life in the ground.

For the high-performance concrete (HPC), the optimum-package storage system of bottom ash (BA)-based dry cement components was identified on the basis of the data on the mechanical strength and cost estimates for the concrete specimens containing the sand and coarse aggregates. The recommended packaging system consisted of the 68.7 wt% BA, 13.0 wt% calcium aluminate cement (CAC), 13.0 wt% Type I portland cement, and 5.3 wt% sodium polyphosphate (NaP). In addition, incorporating a proper amount of polyborax additive into them was required to delay the setting time of the HPC slurries. The slurries were left for 20 hours in a steam at 80°C to obtain a maximum strength of the specimens in a short curing time. The steam-cured HPC specimens has the following mechanical properties; compressive strength of 3980 psi, tensile splitting of 416 psi, flexural strength of 808 psi, and modulus of elasticity of 3.16×10^6 psi. These mechanical strengths were much higher than those for the conventional Type I cement-based concrete specimens cured in the same way. Furthermore, HPC specimens displayed a better resistance to acid erosion and a lower permeability of water, compared with those of the Type I cement concrete specimens. This information strongly verified that the BA-

based HPC has a high potential for use in the precast concrete products, such as building blocks, pipes, and slabs.

Reference

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Table 1. Elemental composition of bottom ash.

<i>Test Parameter</i>	<i>Result</i>	<i>Units</i>	<i>Analysis Method</i>
Arsenic (As) **	178	mg/Kg dry wt.	EPA 208.2
Barium (Ba) **	721	mg/Kg dry wt.	EPA 208.1
Cadmium (Cd) **	<0.20	mg/Kg dry wt.	EPA 213.1
Calcium	42900	mg/Kg dry wt.	SW 846; 6010B
Chromium (Cr) **	22.5	mg/Kg dry wt.	EPA 218.2
Copper (Cu) **	1610	mg/Kg dry wt.	EPA 220.1
Iron (Fe) **	12000	mg/Kg dry wt.	EPA 238.1
Lead (Pb) **	264	mg/Kg dry wt.	EPA 239.1
Loss on Ignition	0.005	% by dry wt	Lab Method
Magnesium (Mg)	35700	mg/Kg dry wt.	SW 846; 6010B
Manganese (Mn) **	336	mg/Kg dry wt.	EPA 243.1
Mercury (Hg) **	<0.25	mg/Kg dry wt.	SW 846; 7471A
Moisture	<0.5	% by wt.	Lab Method
Nickel (Ni) **	11600	mg/Kg dry wt.	EPA 249.1
Selenium (Se) **	12	mg/Kg dry wt.	EPA 270.2
Vanadium (V) **	86700	mg/Kg dry wt.	EPA 286.1
Zinc (Zn) **	3070	mg/Kg dry wt.	EPA 289.1

Table 2. Formulations of WWTS-based PEA used as remediating materials for Pb-contaminated soil.

NaP concentration, wt%	WWTS, wt%	Type I cement, wt%	NaP solution, wt%	Soil, wt%
0	21	9	39	31
10	21	9	40	30
20	20	9	42	29
30	19	8	46	27
40	18	8	48	26

Table 3. Leachability of Ni, V, and Pb metals and compressive strength for PEA specimens.

Concentration of NaP, wt%	Compressive strength, psi	TCLP leachability, mg/L		
		Ni	V	Pb
0	20	0.62	14.8	< 0.004
10	70	0.54	31.0	0.017
20	140	0.65	101.0	0.018
30	190	10.8	122.0	< 0.004
40	220	2.95	185.0	< 0.004

Table 4. Infield leachability of Pb, Ni, and V metals for 25-day-aged PEA-treated and untreated soil specimens after placement.

Infield leachability , mg/l					
Untreated soil			PEA-treated soil		
Pb	Ni	V	Pb	Ni	V
26.4	0.56	0.88	0.74	3.52	11.0

Table 5. Formulations of BA- and NBA-based concrete specimens.

Binder/ag- gregate ratio	Binder phase			Aggregate phase*		40wt% NaP solution, wt%
	BA, wt%	NBA, wt%	CAC, wt%	CA, wt%	FA, wt%	
30/70	18	-	8	31	31	13
40/60	24	-	10	25	25	16
50/50	30	-	12	21	21	16
60/40	35	-	15	17	17	16
30/70	-	18	8	30	30	15
40/60	-	23	10	25	25	17
50/50	-	29	12	20	20	19
60/40	-	33	14	16	16	21

* CA: coarse aggregate

FA: fine aggregate

Table 6. Changes in compressive strength for the concrete specimens cured in steam at 80°C as a function of binder/aggregate ratio.

BA binder/aggregate ratio	NBA binder/aggregate ratio	Compressive strength, psi
30/70	-	3180
40/60	-	3362
50/50	-	3536
60/40	-	3339
-	30/70	1620
-	40/60	1950
-	50/50	2000
-	60/40	1820

Table 7. Formulations of dry mix BA-based cement/aggregate packaging.

Specimen No.	Formulation, wt%				
	BA	CAC	NaP	CA*	FA**
104	33.3	14.3	4.8	23.8	23.8
105	32.6	14.0	7.0	23.2	23.2
106	31.9	13.6	9.1	22.7	22.7
107	31.2	13.3	11.1	22.2	22.2

*CA: coarse aggregate

**FA: fine aggregate

Table 8. Compressive strength for the concrete specimens cured in steam at 80°C.

Specimen No.	Concentration of NaP, wt%	Compressive strength, Psi
104	4.8	2640
105	7.0	3650
106	9.1	3260
107	11.1	2890

Table 9. Formulations of cement concrete specimens.

Specimen No.	Formulation*						
	BA wt%	CAC wt%	NaP wt%	Type I wt%	CA wt%	FA wt%	Water wt%
1	29.8	12.8	6.3	-	21.3	21.3	8.5
2	-	-	-	40.8	20.4	20.4	18.4

* BA: bottom ash
CAC: calcium aluminate cement
NaP: sodium polyphosphate
Type I: type I portland cement
CA: coarse aggregate
FA: fine aggregate

Table 10. Compressive strengths of bottom ash-based cement and Type I-based cement concrete specimens cured in water and steam.

Specimen No.	Compressive strength, psi, for specimens cured in water					Compressive strength, psi, for specimens cured in steam for 12 hours at 80°C
	1 day	3 days	7 days	14 days	28 days	
1	1050	2090	2730	3772	3750	3960
2	870	1860	2240	3340	3500	3660

Table 11. Formulations and costs of dry BA-based cement packaging.

Specimen No.	Formulation*, wt%				Cost**, ¢/lb
	BA	CAC	Type I	NaP	
Control	0.0	0.0	100.0	0.0	6.00
1	60.9	26.2	0.0	12.9	12.04
2	62.5	21.4	5.5	10.7	10.34
3	64.1	16.6	11.0	8.4	8.58
4	67.5	13.0	13.0	6.5	7.04
5	68.7	13.0	13.0	5.3	6.32
6	69.3	13.0	13.0	4.7	5.96
7	67.0	8.5	20.2	4.3	5.47
8	68.9	3.0	26.6	1.6	3.42
9	70.0	0.0	30.0	0.0	2.22

*BA : bottom ash.

CAC : calcium aluminate cement.

Type I : type I portland cement.

NaP : sodium polyphosphate.

** BA : 0.6 ¢/lb [4.35 ¢/lb (crushing fee) - 3.75 ¢/lb (disposal cost)].

CAC : 15.0 ¢/lb.

Type I : 6.0 ¢/lb.

NaP : 60.0 ¢/lb.

Table 12. Compressive strength of the specimens cured in steam for 12 hours at 80°C.

Specimen No.	Compressive strength, psi
Control	2965
1	3280
2	3762
3	3938
4	4910
5	4620
6	4380
7	2240
8	1600
9	1210

Table 13. Effect of polyborax admixture in retarding the setting time and in developing the compressive strength of BA-based cement slurries at 25°C.

Polyborax retarder, wt%	Setting time	Compressive strength, psi
0	3 min 15 sec	4500
2.5	6 min 10 sec	4700
3.5	9 min 40 sec	4750
6.0	23 min 5 sec	3900

Table 14. Optimized dry cement packaging.

Formulation*			
BA, wt%	CAC, wt%	Type I, wt%	NaP, wt%
68.7	13.0	13.0	5.3

BA: bottom ash

CAC: calcium aluminate cement

Type I: Type I portland cement

NaP: sodium polyphosphate

Table 15. Formulations of BA- and Type I-based cement concrete specimens.

Cement	Formulation*						
	BA wt%	CAC wt%	Type I wt%	NaP wt%	CA wt%	FA wt%	Water wt%
BA	30.5	5.8	5.8	2.4	22.1	22.1	11.3
Type I	-	-	40.5	-	20.1	20.1	19.3

*BA: bottom ash

CAC: calcium aluminate cement

Type I: Type I portland cement

NaP: sodium polyphosphate

CA: coarse aggregate

FA: fine aggregate

Table 16. Compressive strength, flexural strength, tensile splitting, and modulus of elasticity of 80°C steam-cured BA- and Type I-based concrete specimens.

Cement	Compressive strength, psi	Flexural strength, psi	Tensile splitting, psi	Modulus of elasticity, $\times 10^6$ psi
BA	3980	808	416	3.16
Type I	3660	525	271	2.65

Table 17. Water absorption of 80°C steam-cured BA- and Type I-based cement concrete specimens after immersion in water at 25°C.

Cement	Water Absorption, wt%		
	7 hours	1 day	7 days
BA	6.53	7.08	8.25
Type I	12.5	12.7	13.38

Table 18. Changes in weight of 80°C steam-cured BA- and Type I- based cement concrete specimens after exposure for up to 10 days to 6 % H₂SO₄ and 6 % NaOH solution at 25°C.

Cement	6 % H ₂ SO ₄		6 % NaOH	
	5 days	10 days	5 days	10 days
BA	- 1.62	- 2.80	- 0.22	- 0.46
Type I	- 4.07	- 8.75	+ 0.04	+ 0.29

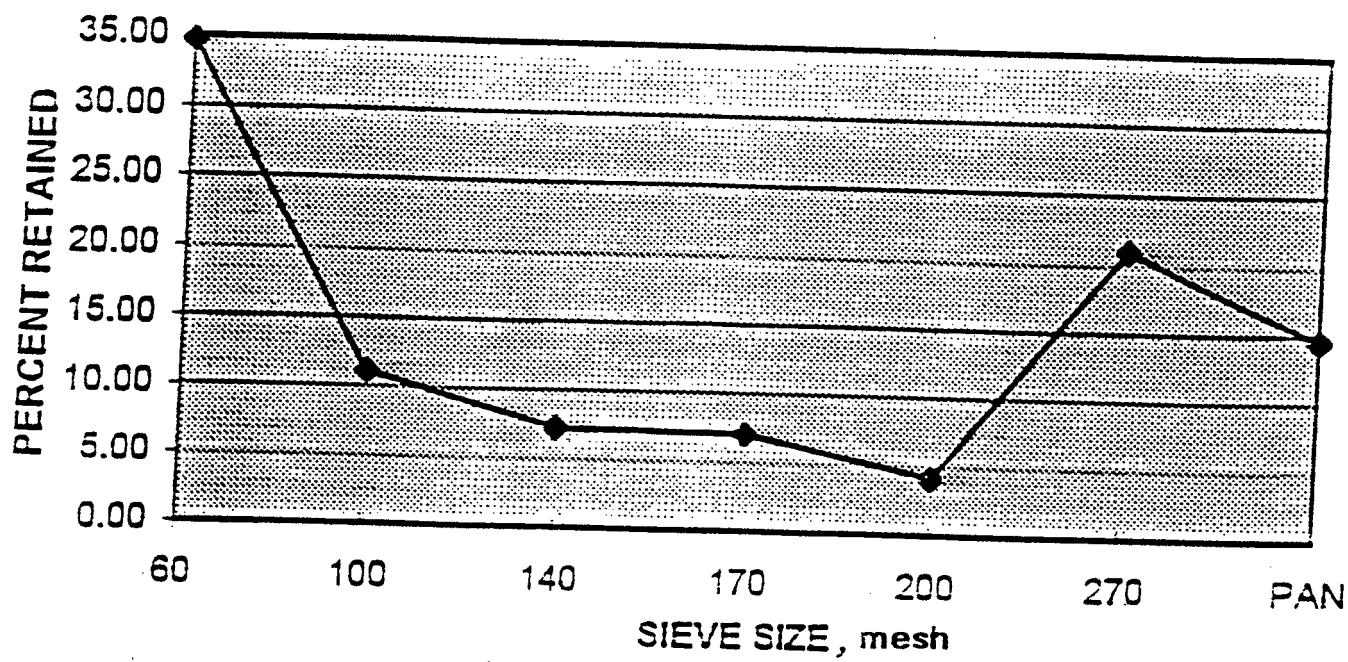


Figure 1. Sieve size of crushed BA powder

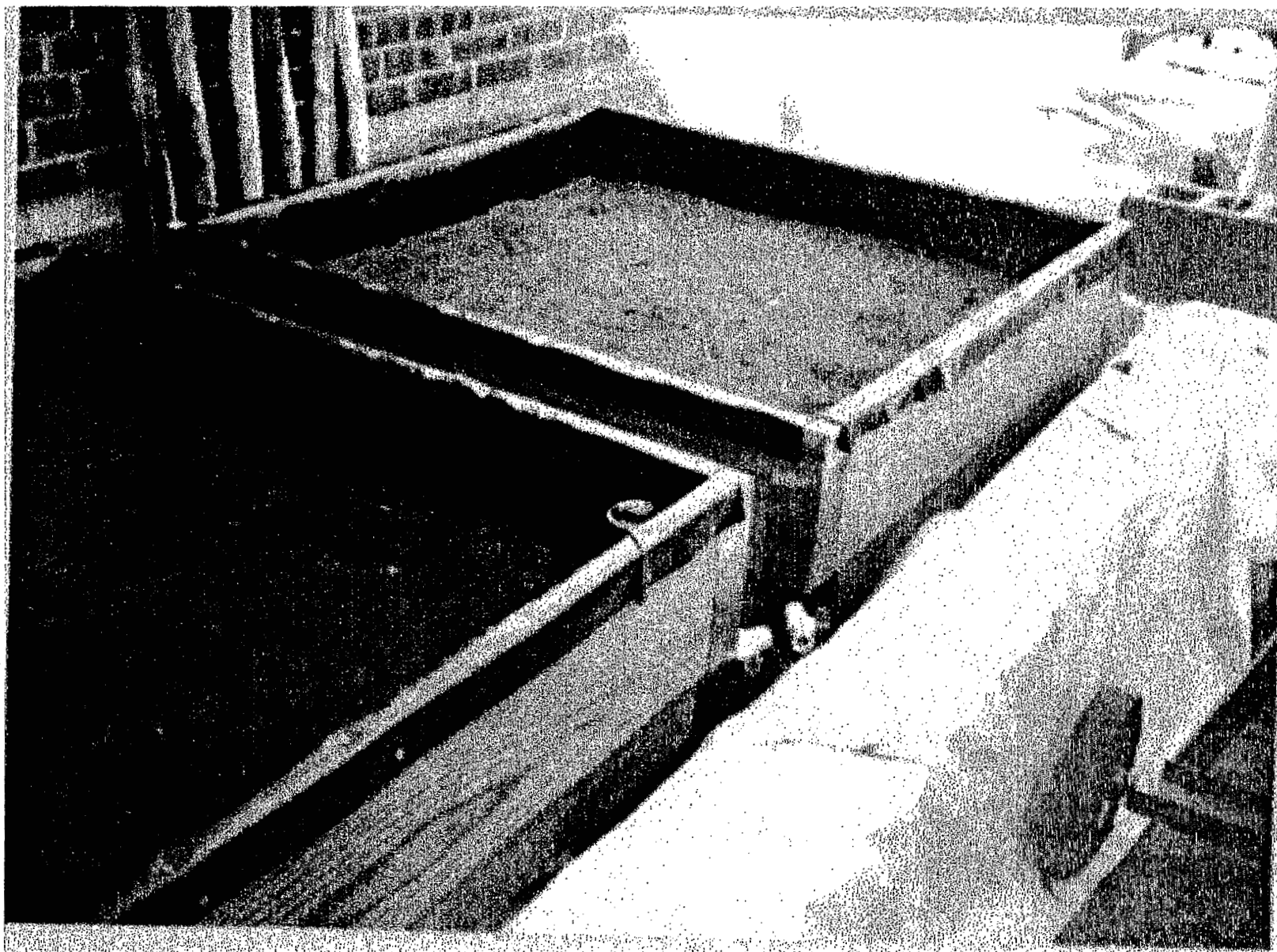


Figure 2. A 186 lb of Pb-contaminated soil placed in each of the two molds (4 ft. x 4ft. x 0.8 ft.)

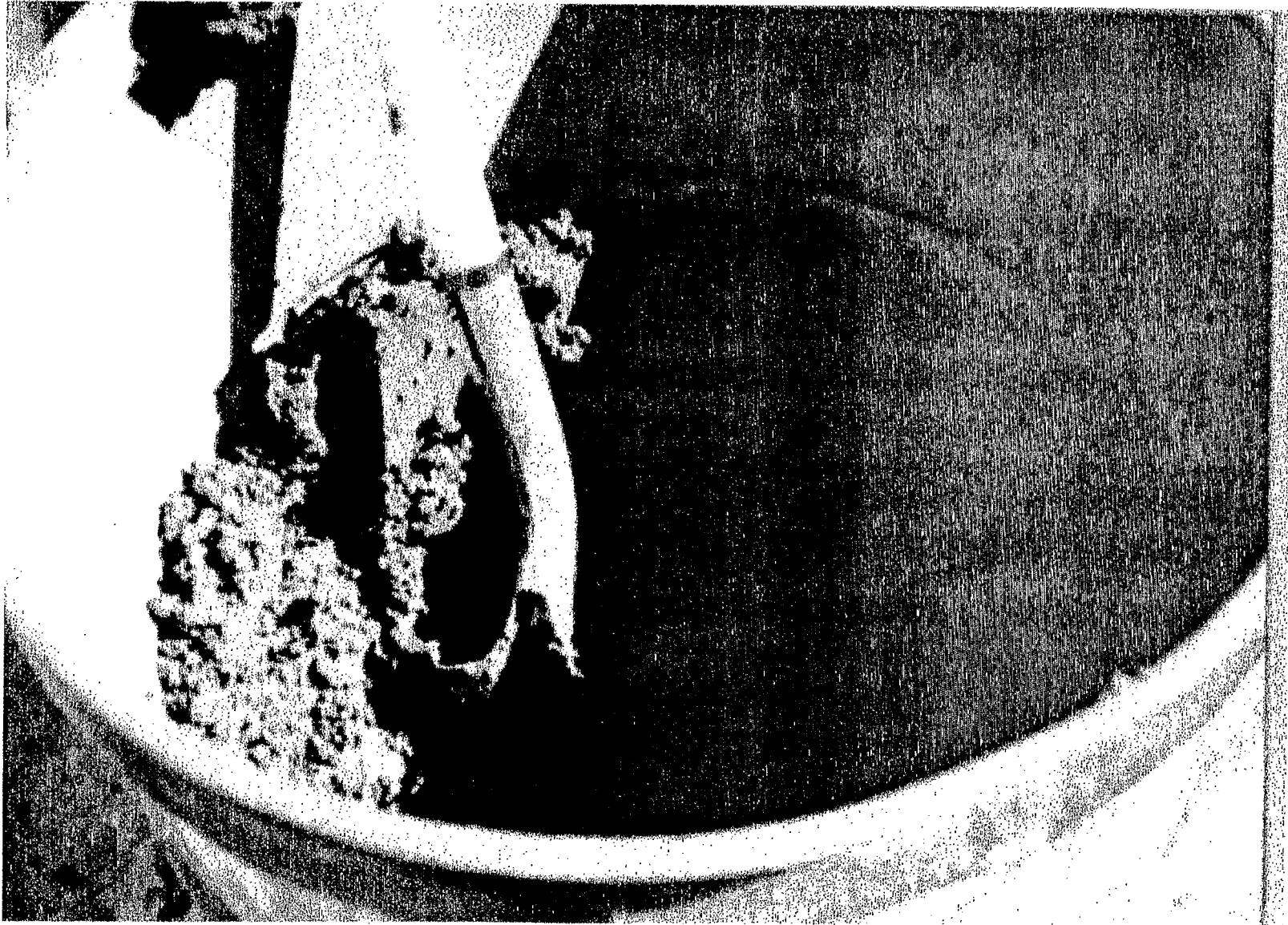


Figure 3. Removing raw WWTS from its storage drum

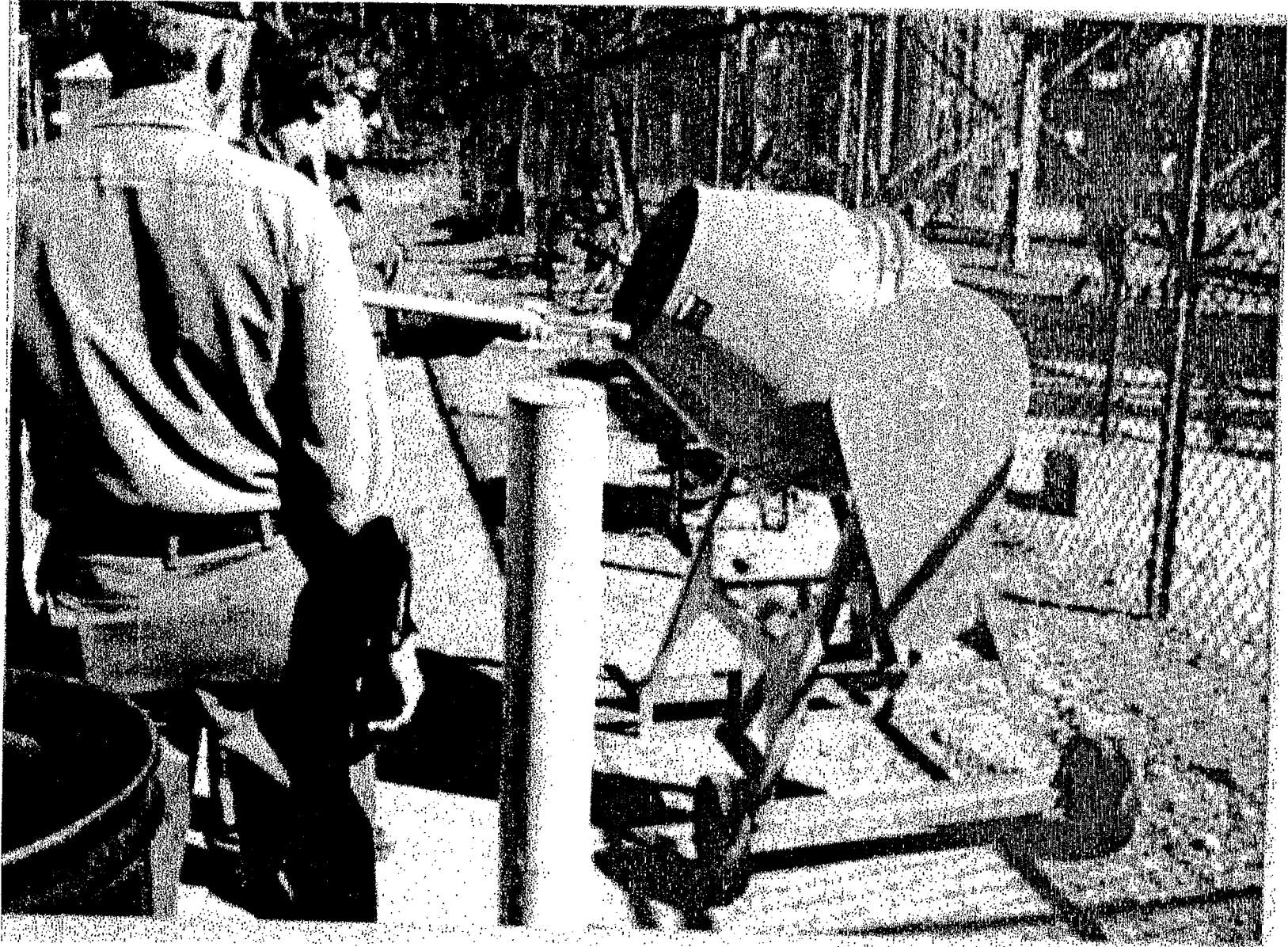


Figure 4. Loading raw WWTS into a rotary shear concrete mixer

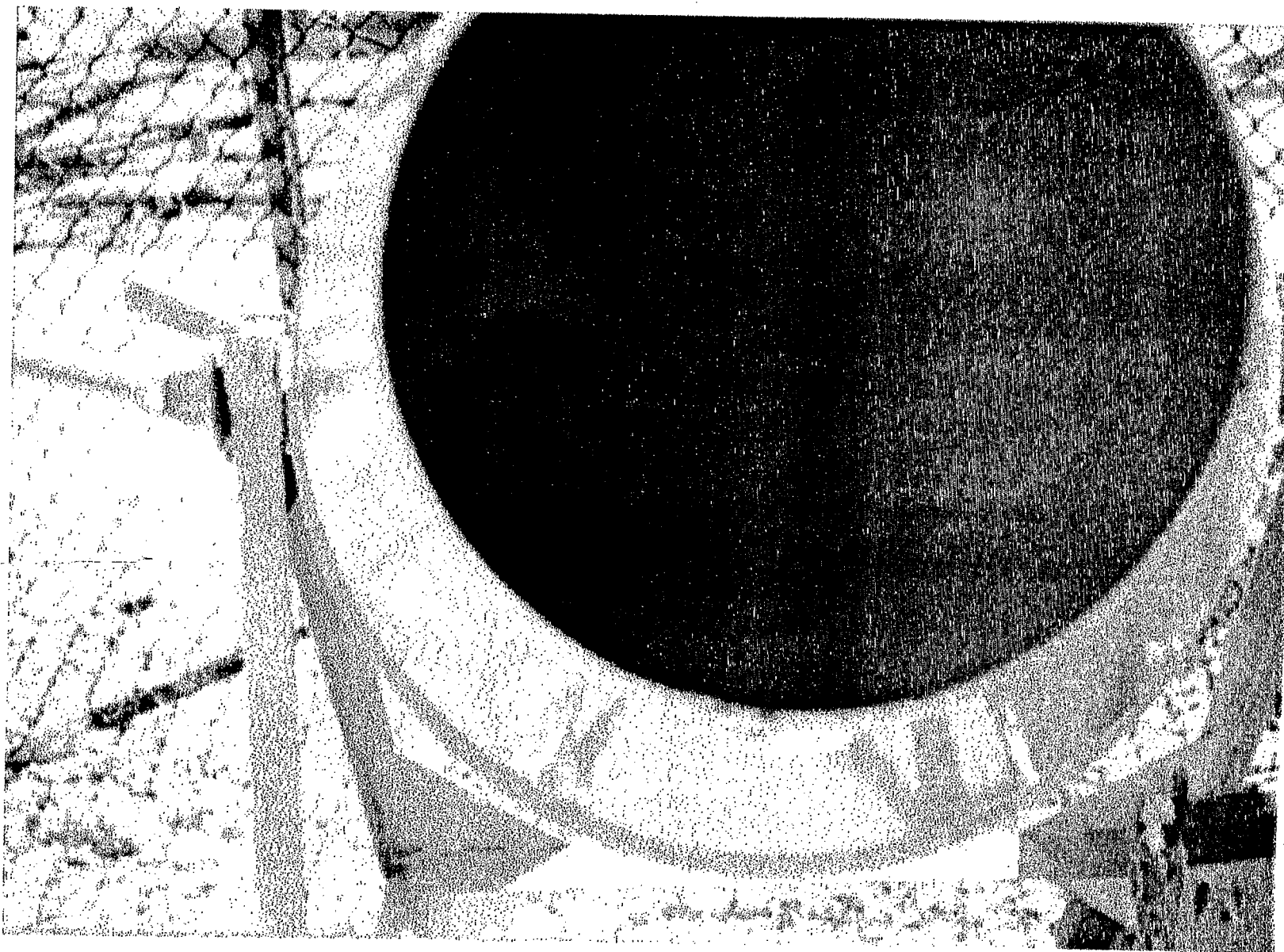


Figure 5. Rotating raw WWTS-loaded mixer



Figure 6. Mixing the WWTs suspension with cement



Figure 7. Discharging the PEA slurry into a plastic pail

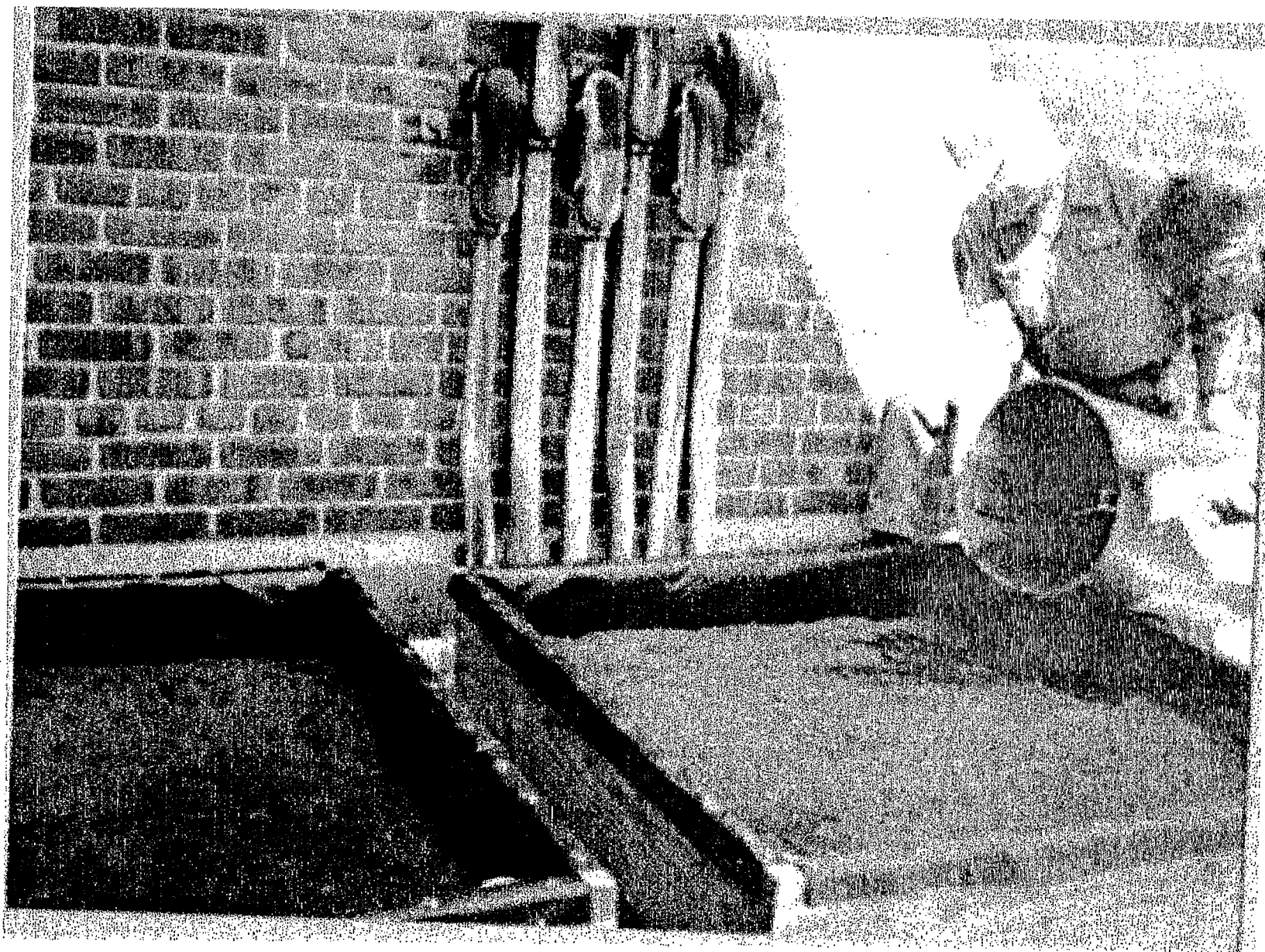


Figure 8. Pouring the PEA slurry onto the surface of Pb-contaminated soil

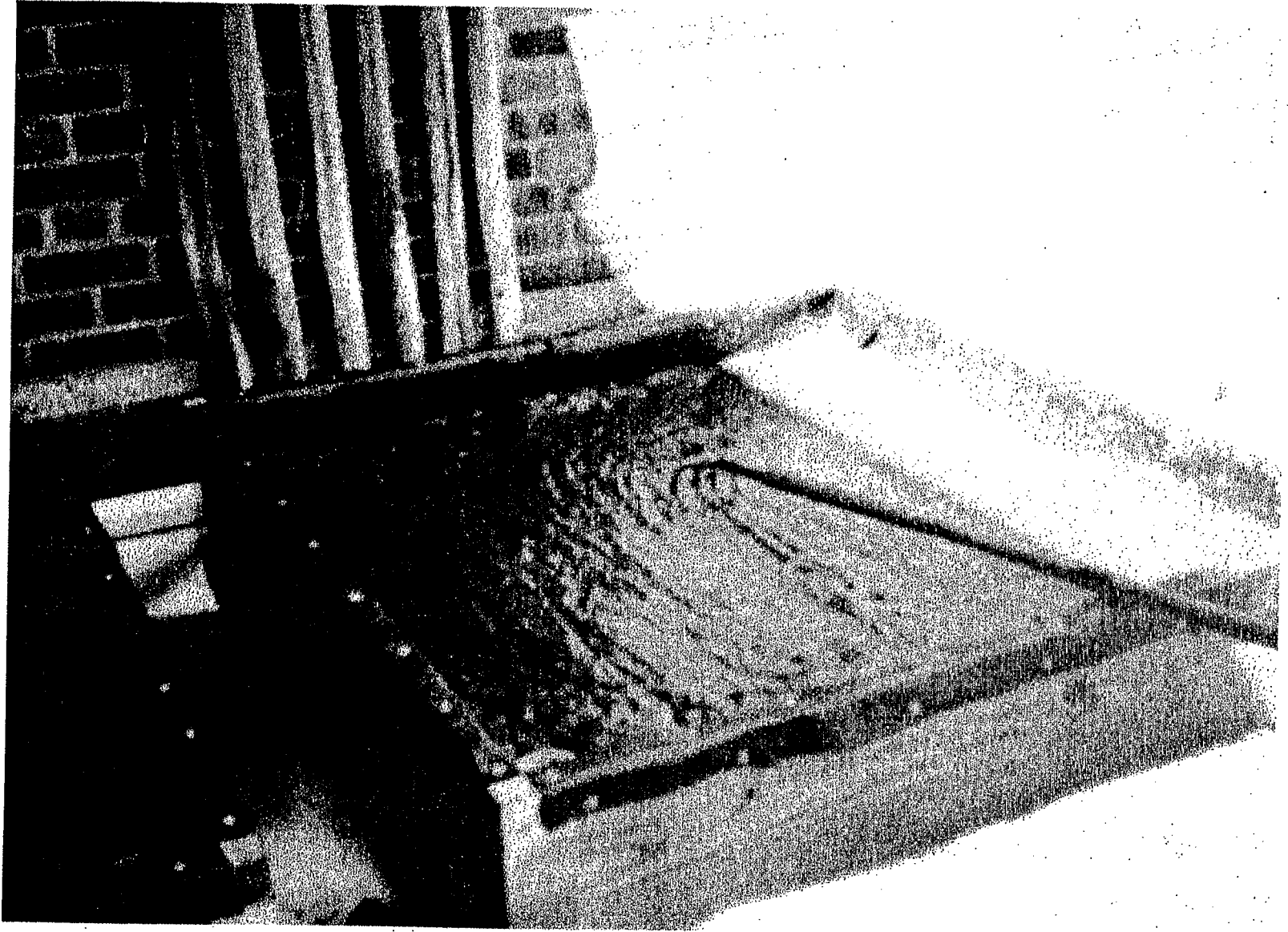


Figure 9. Blending the PEA slurry with contaminated soil using a claw tool

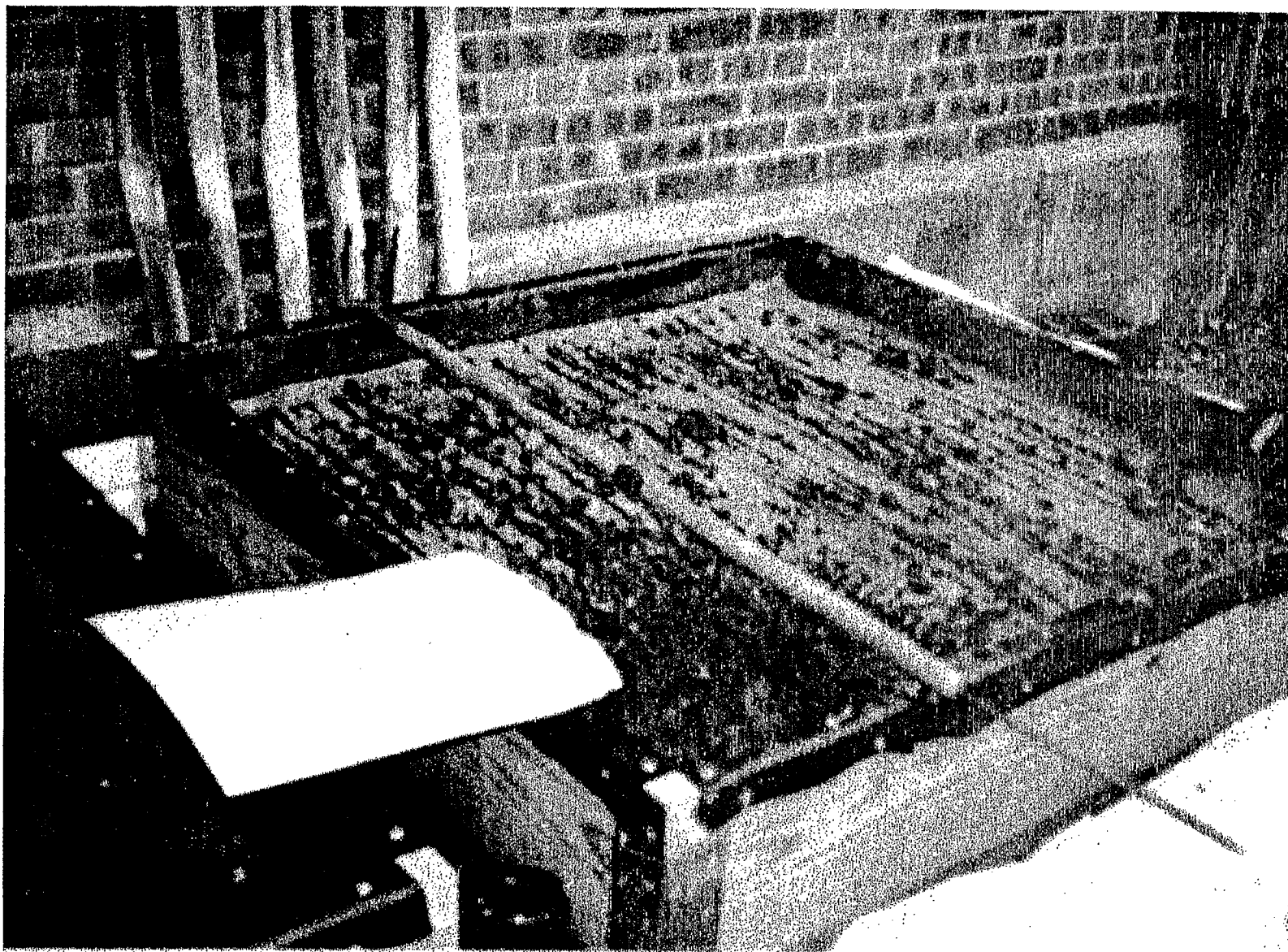


Figure 10. Surface of a 7-day-aged PEA-treated soil specimen scratched by a claw tool

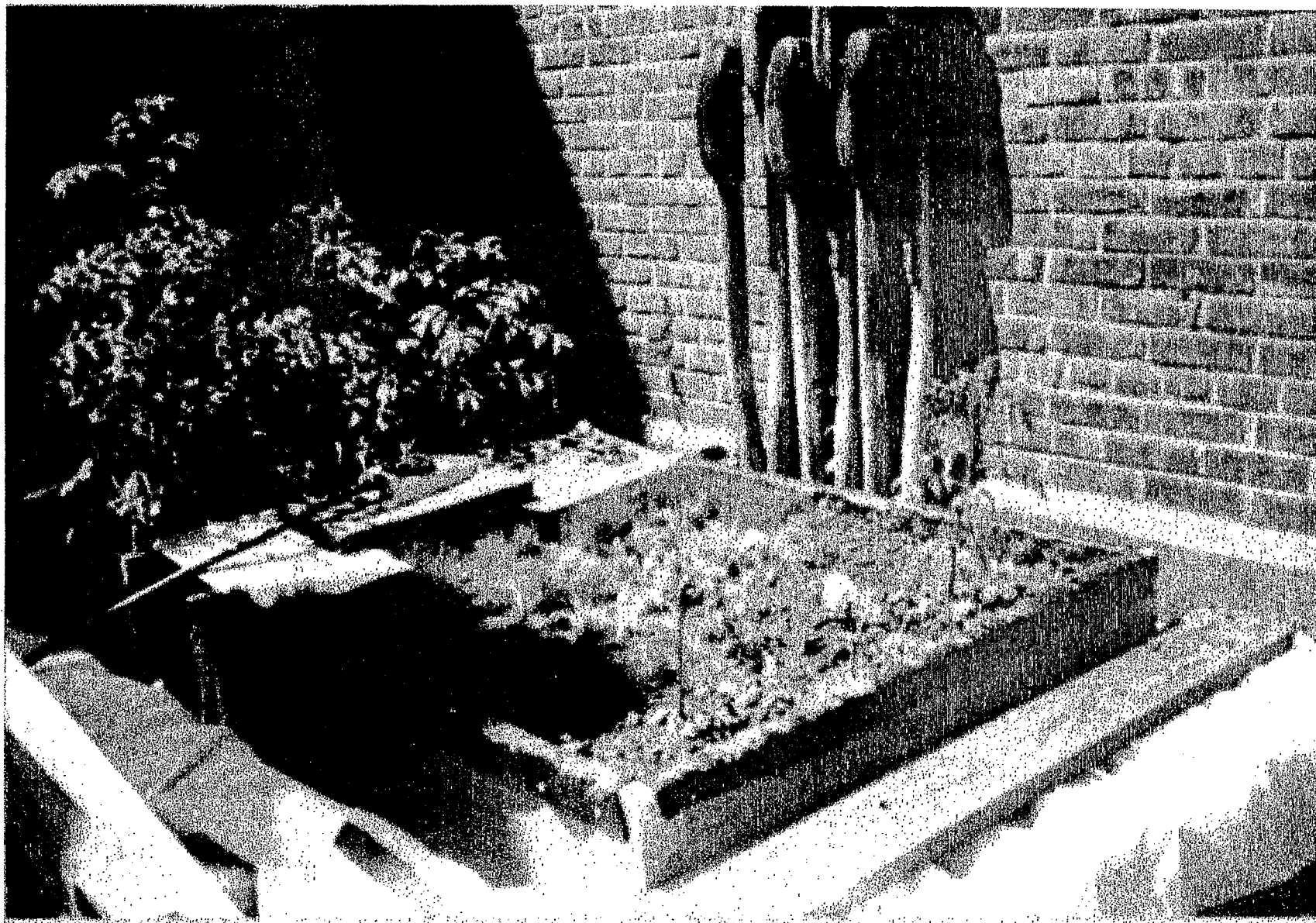


Figure 11. Growth of plants in PEA-treated (right side) and untreated soils (left side) after a month